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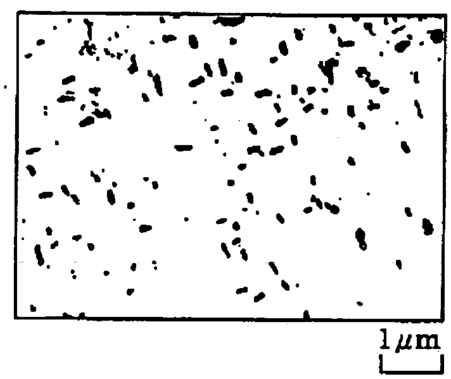
(54) Stainless steel improved in anti-microbial property and manufacturing thereof

(57) Stainless steel is improved in anti-microbial property by the addition of Cu in amount of 0.4-5.0 wt.% and the precipitation of Cu-rich phase at the ratio of 0.2 vol.% or more. The Cu-rich phase is precipitated as minute particles uniformly dispersed in the matrix not only at the surface layer but also at the interior by such heat treatment as annealing or aging at 500-900°C. Since the anti -microbial property is derived from the material itself, the stainless steel does not lose the excellent anti-microbial property even after polished or mechanically worked. Due to the anti-microbial property, the stainless steel is useful as material in various fields requiring sanitary environments, e.g. kitchen goods, electric home appliances, devices or tools at hospitals, parts or interiors for building and grips or poles for electric trains or busses.

FIG.1



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Description

The present invention is related to stainless steel improved in anti-microbial, and also related to a method of manufacturing thereof.

Stainless steel represented by SUS 304 has been used as kitchen goods, various devices or tools at hospitals, interior parts for building, grips or poles provided in public transport vehicles, e.g. busses or electric trains. However, in these days when hospital infection caused by Staphylococcus aureus becomes serious problems, it has been demanded that the material for such use shall have the anti-microbial property which unnecessitates periodical disinfection.

Anti-microbial property can be obtained by forming an organic film or an anti-microbial coating layer, as disclosed in Japanese Patent Applications Laid-Open 8-53738 and 8-225895.

However, such the anti-microbial film or layer has the disadvantage that anti-microbial function disappears in response to the consumption of the film or layer. Besides, the organic film which lost the anti-microbial function would serve as the nutrition source to promote the propagation of bacilli or germs on the contrary.

The complex plating layer containing an antimicrobial component shows poor adhesiveness to a substrate, so that the coated substrate is inferior in workability. The external appearance and anti-microbial function become worse due to the dissolution, abrasion and defects of the plating layer.

By the way, it is well known that metal element such as Ag or Cu exhibits effective anti-microbial function. However, Ag is expensive and unsuitable for a part to be used in a corrosive atmosphere. On the other hand, Cu is relatively cheap element and effective as an anti-microbial agent. In this regard, it has been investigated to apply anti-microbial function to material such as stainless steel by the addition of Cu.

The inventors has been researched and examined the effect of Cu on the improvement of antimicrobial property, and invented that anti-microbial function is enhanced by increasing the concentration of Cu in the surface layer of stainless steel, as disclosed in Japanese Patent Applications Laid-Open 6-209121 and 7-55069.

The present invention is accomplished aiming at the further enhancement of such Cu effect.

The object of the present invention is to apply excellent anti-microbial property to stainless steel by precipitating a secondary phase mainly composed of Cu (hereinafter referred to as "Cu-rich phase") at a predetermined ratio.

The stainless steel according to the present invention contains 0.4-5.0 wt.% Cu and has the structure that Cu-rich phase is dispersed in the matrix at the ratio of 0.2 vol.% or more. The Cu-rich phase is precipitated by heat treatment such as aging or annealing at a temperature specified in relation with the kind of the stainless steel, i.e. ferritic, austenitic or martensitic type.

The ferritic stainless steel has the composition containing 0.1 wt.% or less C, 2 wt.% or less Si, 2 wt.% or less Mn, 10-30 wt.% Cr, 0.4-3 wt.% Cu, optionally 0.02-1 wt.% Nb and/or Ti and the balance being Fe. This stainless steel may further contain at least one of Mo up to 3 wt.%, Al up to 1 wt.%, Zr up to 1 wt.%, V up to 1 wt.%, B up to 0.05 wt.% and rare earth metals (REM) up to 0.05 wt.%.

When such the ferritic stainless steel is aged at 500-800 °C, Cu-rich phase is precipitated at the ratio of 0.2 vol.% or more. The aging treatment is performed, after the stainless steel is cold rolled and then finally annealed.

The austenitic stainless steel has the composition containing 0.1 wt.% or less C, 2 wt.% or less Si, 5 wt.% or less Mn, 10-30 wt.% Cr, 5-15 wt.% Ni, 1.0-5.0 wt.% Cu, otpionally 0.02-1 wt.% Nb and/or Ti and the balance being essentially Fe. This stainless steel may further contain one or more of Mo up to 3 wt.%, Al up to 1wt.%, Zr up to 1 wt.%, V up to 1 wt.%, B up to 0.05 wt.% and rare earth metals (REM) up to 0.05 wt.%.

When such the austenitic stainless steel is heat treated at 500-900 °C at least one time, Cu-rich phase is precipitated at the ratio of 0.2 vol.% or more. The heat treatment may be performed on any stage in the process line from hot rolling before the formation of a final product.

The martensitic stainless steel has the composition containing 0.8 wt.% or less C, 3 wt.% or less Si, 10-20 wt.% Cr, 0.4-5.0 wt.% Cu and the balance being essentially Fe. This stainless steel may further contain one or two of Mo up to 4 wt.% and V up to 1 wt.%.

In this case, Cu-rich phase can be precipitated by the batch-type annealing where a hot-rolled steel sheet is heated one hour or longer at 500-900 °C. Thereafter, the steel sheet may be further cold rolled and then finally annealed at 700-900°C.

Fig. 1 shows the metallurgical structure of a Cu-containing ferritic stainles steel aged 1 hour at 800°C observed by a transmission electron microscope.

Stainless steel is good of corrosion resistance in general, since it is coated with a hydroxide layer mainly composed of Cr (so-called "passive film"). The inventors measured the concentration of Cu included in the passive film formed on the ferritic stainless steel containing Cu effective for anti-microbial function, and researched the anti-microbial property by the examination using *Staphylococcus aureus*-containing liquid. It is noted that although anti-microbial property is improved by the addition of Cu to the steel, the anti-microbial function and its persistency are ocasionally insufficient only by dissolving a few % Cu in the steel.

The inventors have advanced the researching on the effect of Cu and found that the precipitation of such Cu-rich

phase as shown in Fig. 1 effectively improves the anti-microbial function. When Cu added to the steel is partially precipitated as said Cu-rich phase at the ratio of 0.2 vol.% or more, the anti-microbial function is remarkably enhanced. The Cu-rich phase may have f.c.c. or h.c.p. structure.

The Cu-rich phase may be precipitated by isothermal heat treatment such as aging at a temperature in the range to facilitate the precipitation of the Cu-rich phase or such slow cooling as holding the steel in the precipitation temperature range for longest possible time. In this point of view, the inventors have further advanced the researching of the effect of heat treatment on the precipitation ratio of the Cu-rich phase. As the results of the researching, it is found that the precipitation of the Cu-rich phase is promoted under different conditions in response to the kind of stainless steel as follows.

In the case of the ferritic stainless steel, the precipitation of the Cu-rich phase is promoted by aging the steel at a temperature in the range of 500-800 °C after final annealing. In the case of the austenitic stainless steel, the precipitation of the Cu-rich phase is promoted by aging the steel at a temperature in the range of 500-900 °C after final annealing. In the case of the martensitic stainless steel, the precipitation of the Cu-rich phase is promoted by the batch-type annealing where the Cu-containing martensitic stainless steel is heated at a temperature in the range of 500-900°C after final annealing. Even when the martensitic stainless steel is cold rolled and then continuously annealed at 700-900 °C in succession to said batch-type annealing, the durability of anti-microbial function is not reduced.

The dispersion of the Cu-rich phase is made more uniform over the whole matrix of the stainless steel by the addition of the other element, e.g. Ti or Nb, which easily forms carbonitride or precipitate. Since such carbonitride or precipitate serves as the precipitation site for the Cu-rich phase, the Cu-rich phase is deposited as minute precipitates uniformly dispersed in the matrix. Consequently, the stainless steel is further improved in anti-microbial function as well as productivity.

[Ferritic Stainless Steel]

The alloying elements and those contents in the ferritic stainless steel according to the present invention will be apparent in the following description.

C improves the strength of the ferritic stainless steel. C serves as the alloying element for effectively promoting the uniform dispersion of the Cu-rich phase due to the formation of chromium carbide, too. However, the excessive addition of C in amount more than 0.1 wt.% would reduce productivity and corrosion resistance. Si is an alloying element effective for improving corrosion resistance and strength, but the excessive addition of Si in amount more than 2 wt.% would reduce productivity. Mn is an alloying element effective for improving productivity and stabilizing harmful S as MnS. However, the excessive addition of Mn in amount more than 2 wt.% would reduce corrosion resistance. Cr is an essential alloying element for maintaining the corrosion resistance of the ferritic stainless steel. The corrosion resistance is ensured by Cr content at 10 wt.% or more. However, the addition of Cr in amount exceeding 30 wt.% would reduce productivity.

Cu is the most important component in the ferritic stainless steel according to the present invention. In order to ensure excellent anti-microbial function, it is necessary to precipitate the Cu-rich phase at the ratio of 0.2 vol.% or more. The precipitation of Cu-rich phase at said ratio requires the addition of Cu in an amount of 0.4 wt.% or more. However, Cu content shall be controlled 3 wt.% or less, otherwise the excessive addition of Cu would cause poor productivity as well as poor corrosion resistance. Although there are no restrictions on the size of Cu-rich phase precipitates, the Cu-rich phase is preferably deposited as minute precipitates uniformly dispersed in the matrix in order to apply anti-microbial function uniformly to the whole surface of a product.

Nb and Ti are optional alloying elements to be added to the ferritic stainless steel, and form the precipitates which serve as seeds to uniformly precipitate Cu-rich phase. These functions appear distinctly, when the steel contains Nb and/or Ti in an amount of 0.02 wt.% or more. However, Nb and/or Ti contents shall be restricted at 1 wt.% or less, since the excessive addition of Nb and/or Ti would reduce productivity or workability.

Mo is an optional alloying element effective in corrosion resistance and strength. However, the excessive addition of Mo in amount more than 3 wt.% would reduce the productivity and workability of the steel. Al is an optional alloying element effectivein corrosion resistance. However, the excessive addition of Al in amount more than 1 wt.% would reduce productivity and workability.

Zr is an alloying element to be added to the steel as occasion demands, and has the function to form carbonitrides effective in the improvement of strength. However, the excessive addition of Zr in amount more than 1 wt.% would reduce the productivity or workability of the steel. V is the same optional alloying element as Zr. However, the excessive addition of V in amount more than 1 wt.% deteriorates the productivity or workability of the steel. B is an optional alloying element effective in the improvement of hot workability. However, the excessive addition of B in amount more than 0.05 wt.% causes the deterioration of hot workability on the contrary. REM are optional alloying elements having the same function as B does. However, the excessive addition of REM in amount more than 0.05 wt.% reduces hot workability on the contrary.

Aging Treatment: at 500-800 °C

When the ferritic stainless steel having the specified composition is aged at 500-800°C, the Cu-rich phase is effectively precipitated. As the steel is aged at a relatively lower temperature, the ratio of Cu dissolved in the matrix becomes smaller, while the ratio of the Cu-rich phase precipitates becomes bigger. However, too lower temperature aging retards the diffusion of elements in the matrix and causes the reduction of the precipitation ratio. We have researched the effect of the aging treatment on the anti-microbial property under various temeprature conditions and reached the conclusion that the temperature range of 500-800°C is industrially the most effective for the precipitation of Cu-rich phase.

[Austenitic Stainless Steel]

The alloying elements and those contents in the austenitic stainless steel according to the present invention will be apparent in the following description.

C is the alloying element which forms chromium carbide effective as the precipitation site for the Cu-rich phase so as to uniformly disperse minute Cu-rich phase precipitates. However, the excessive addition of C more than 0.1 wt.% would cause the reduction of productivity and corrosion resistance. Si is an alloying element effective for improving corrosion resistance as well as anti-microbial function. However, the excessive addition of Si in amount more than 2 wt. % would cause poor productivity. Mn is an alloying element effective for improving productivity and stabilizing harmful S as MnS in the steel. In addition, MnS serves as the precipitation site of the Cu-rich phase so as to minutely precipitate the Cu-rich phase. However, the excessive addition of Mn in amount more than 5 wt.% would reduce corrosion resistance. Cr is an essential alloying element for ensuring the corrosion resistance of the austenitic stainless steel. Cr content in amount of 10 wt.% or more is necessary in order to obtain sufficient corrosion resistance. However, the excessive addition of Cr in amount more than 30 wt.% would reduce productivity and workability. Ni is an alloying element necessary for the stabilization of austenitic phase. However, the excessive addition of Ni means the consumption of expensive Ni in large amount, and raises the cost of the steel. In this regard, Ni content is controlled 15 wt.% or less.

Cu is the most important component in this austenitic stainless steel according to the present invention. In order to obtain sufficient anti-microbial function, the Cu-rich phase shall be precipitated at the ratio of 0.2 vol.% or more. Said precipitation in the austenitic stainless steel necessitates the addition of Cu in amount of 1.0wt.% or more. However, the excessive addition of Cu in amount more than 5.0 wt.% would reduce productivity, workability and corrosion resistance. There are no restriction on the size of Cu-rich phase precipitates. However, the proper dispersion and distribution of the precipitated Cu-rich phase in both of the surface layer and the interior is preferable to exhibit anti-microbial function uniformly over the whole surface of a steel product and to keep sufficient anti-microbial function even when the surface layer is polished.

Nb forms carbide, nitride and/or carbonitride dispersed in the matrix. These precipitates effectively promotes the minute and uniform dispersion of the Cu-rich phase in the matrix, since the Cu-rich phase is likely to precipitate around the precipitates. However, the excessive addition of Nb would reduce productivity and workability. Therefore, Nb content is preferably controlled in the range of 0.02-1 wt.%, when Nb is added to the steel. Ti has the same function as Nb does. However, since the addition of Ti in excessive amount reduces productivity or workability, scratches would be easily formed on the surface of an obtained product. In this regard, Ti content is preferably controlled in the range of 0.02-1 wt.%, when Ti is added to the steel.

Mo is an optional alloying element effective for improving corrosion resistance. Mo forms the intermetallic compounds such as Fe_2Mo which serve as the precipitation site of the Cu-rich phase, too. Mo as well as the Mo-containing compounds are also effective in the improvement of anti-microbial function. However, the addition of Mo in excessive amount more than 3 wt.% would reduce productivity and workability. Al is an otional alloying element effective for improving corrosion resistance and for minutely precipitating the Cu-rich phase. However, the addition of Al in excessive amount more than 1 wt.% would reduce productivity or workability. In this regard, Al content shall be controlled to 1 wt.% or less, when Al is added to the steel. Zr is the optional alloying element which forms carbonitrides effective for the minute precipitation of the Cu-rich phase. However, the addition of Zr in excessive amount more than 1 wt.% would reduce productivity or workability. V is the optional alloying element which forms carbonitirdes as the same as Zr does, so as to facilitate the minute precipitation of the Cu-rich phase. However, the excessive addition of V in amount more than 1 wt.% would reduce productivity or workability. B is an optional alloying element effective for improving hot workability and forming precipitates uniformly dispersed in the matrix. However, the addition of B in excessive amount more than 0.05 wt.% would reduce hot workability. REM are optional alloying elements. When REM in proper amount are added to the steel, the steel is improved in hot workability. In addition, REM form precipitates, effective for the minute precipitation of the Cu-rich phase, uniformly dispersed in the matrix. However, the addition of REM in excessive amount more than 0.05 wt.% would reduce hot workability.

When the austenitic stainless steel having the specified composition is heat treated at 500-900°C, the Cu-rich phase is effectively precipitated in the matrix at the ratio of 0.2 vol.% or more. As the heating temperature bewcomes relatively lower, the ratio of Cu dissolved in the matrix is reduced, while the precipitation ratio of the Cu-rich phase is

increased. However, heating at a too lower temperature retards the diffusion of elements in the steel and reduces the precipitation ratio. We have searched and examined the effect of aging treatment on anti-microbial property under various temperature conditions, and reached the conclusion that one hour or longer aging treatment at a temperature in the range of 500-900 °C is industrially advantageous. The aging treatment may be applied to the steel on any stage in the process line from hot rolling until the formation of a final product.

[Martensitic Stainless Steel]

The alloying elements and those contents in the martensitic stainless steel according to the present invention will be apparent in the following description.

C is an alloying element effective for improving the strength of the quench-tampered martensitic stainless steel. C forms the chromium carbide which serves as the precipitation site of a Cu-rich phase so as to uniformly disperse minute Cu-rich precipitates in the matrix. However, the excessive addition of C in amount more than 0.8 wt.% would reduce corrosion resistance or ductility. Si is an alloying element effective as a deoxidizing agent and has the function to improve temper softening resistance and anti-microbial property. These effects are increased up to 3.0 wt.% Si, but not enhanced any more even when Si in amount more than 3 wt.% is added to the steel. Cr is an alloying element necessary for the corrosion resistance of the martensitic stainless steel. Cr content shall be controlled to 10 wt.% or more in order to ensure corrosion resistance necessary for use. However, the excessive addition of Cr in amount more than 20 wt.% would reduce the hardness of the quenched steel and cause poor workability and ductility due to the formation of coarse eutectic carbide.

Cu is the most important component in the martensitic stainless steel according to the present invention. In order to obtain sufficient anti-microbial function, Cu-rich phase shall be precipitated at the ratio of 0.2 vol.% or more. Said precipitation in the martensitic stainless steel necessitates the addition of Cu in amount of 0.4 wt.% or more. However, the excessive addition of Cu in amount more than 5.0 wt.% would reduce productivity, workability and corrosion resistance.

There are no restrictions on the size of Cu-rich phase precipitates. However, the proper dispersion and distribution of the Cu-rich phase in both of the surface layer and the interior is preferable to exhibit anti-microbial function uniformly over the whole surface of a steel product and to keep sufficient anti-microbial function even when the surface layer is polished.

Mo is an optional alloying element effective for improving corrosion resistance. Mo forms the intermetallic compounds such as Fe_2Mo which serve as the precipitation site to facilitate the minute dispersion of the Cu-rich phase. In addition, Mo and Mo-containing compounds themselves effectively improve anti-microbial property. However, the excessive addition of Mo in amount more than 4 wt.% would reduce productivity and workability. An optional alloying element V forms the carbide which serves as the precipitation site to facilitate the minute precipitation of Cu-rich phase. The formation of cabide is effective in the improvement of abrasion resistance and temper softening resistance, too. However, the excessive addition of V in amount more than 1 wt.% would reduce productivity and workability.

The martensitic stainless steel may further contain one or more of Nb up to 0.5 wt.%, Ti up to 1.0 wt.% and Ta or Zr up to 0.3 wt.% to contribute the formation of fine crystal grains effective in low-temperature toughness, Al up to 1.0 wt.% and W up to 2.0 wt.% to improve temper-softening resistance, Ni up to 2.0 wt.% effective in the improvement of strength and toughness, and B up to 0.01 wt.% to improve hot workability.

When the martensitic stainless steel having the specificed composition is subjected to batch-type annealing, the Cu-rich phase is precipitated in the matrix. The ratio of Cu dissolved in the matrix becomes smaller as the lowering of an annealing temperature. However, a too lower temperature retards the diffusion of elements in the steel, so that the precipitation ratio is reduced on the contrary. The inventors have researched the effect of annealing condition on anti-microbial function and reached the conclusion that the annealing temperature of 500-900°C is industrially the most effective in anti-microbial property. The annealing shall be continued at least one hour.

The Cu-rich phase precipitated in the matrix during annealing the hot rolled steel sheet is increased but not reduced in amount, when the steel sheet is subjected to final annealing at 700-900 °C. Therefore, the steel sheet may be intermediately annealed at a temperature in the range of 700-900 °C, although the process according to the present invnetion basically comprises the steps of one cold rolling step and one annealing step.

EXAMPLE

Example 1:

Ferritic stainless steel each having the composition shown in Tables 1 and 2 was melted in a 30kg-vacuum melting furnace, forged, hot rolled and then annealed. The obtained hot rolled sheet was repeatedly subjected to cold rolling and annealing, and finally formed to an annealed cold rolled sheet of 0.5-1.0 mm in thickness. A part of the steel sheets obtained in this way were further subjected to 1 hr. aging treatment.

Test pieces prepared from these steel sheets were observed by a transmission electron microscope (TEM). For

instance, the uniform and minute dispersion of the Cu-rich phase was detected in a thin film sample obtained from the test piece of steel K4 aged 1 hr. at 800 °C, as shown in Fig. 1, and excellent anti-microbial function was noted as far as the steel had the structure wherein the Cu-rich phase was uniformly and minutely dispersed. The precipitation of the Cu-rich phase was quantitatively measured by the microscopic observation.

The anti-microbial examination was done as follows:

(1) Test organisms

Escherichia coli IFO3301
Staphylococcus aureus IFO12732

(2) Preparation of cell suspensions

Each test organism was grown on Nutrient Broth (offered by Eiken Chemical Co., Ltd.) for 16-20 hrs. at 35°C with shaking. After incubation, each culture was diluted 20,000 fold with a phosphate buffer, to use as the cell suspension for the test.

(3) Experimental procedure

A 1-ml portion of each cell suspension was dropped on the surface of each sample (5x5cm), which was incubated at 25 °C. The viable cells of each sample were copunted after 24 hrs. of incubation. A 1-ml portion of each cell suspension dropped in a petridish was used as a control sample, which was tested in the same way.

(4) Viable cell counts

The sample and the control sample were each washed out with 9-ml of SCDLP (Soybean-Casein Digest Broth with Lecithin & Polysorbate) medium (offered by Nihon Pharmaceutical Co., Ltd.). Viable cells in the washing were counted by the pour plate method (incubated at 35°C for 48 hrs.) with Plate Count Agar (offered by Eiken Chemical Co., Ltd.). The viable cells per sample or control sample were calculated from the count of each washing.

The examination results were evaluated and classified as follows: The mark ◎ represents the case where any living microbes were not detected, the mark ○ represents the case where microbes were sterilized at the ratio of 95% or more in comparison with the reference value, the mark Δ represents the case where microbes were sterilized at the ratio of 60-90%, and the mark X represents the case where microbes were sterilized at the ratio not more than 60%.

The evaluation together with the precipitation of Cu-rich phase is shown in Tables 1 and 2.

TABLE 1: THE EFFECT OF THE COMPOSITION OF FERRITIC STAINLESS STEEL AND AGING TREATMENT ON PRECIPITATION RATIO OF Cu-RICH PHASE AND ANTI-MICROBIAL PROPERTY

(THE PRESENT INVENTION)

STEEL	ALLOYING COMPONENTS (wt.%)										AGING TEMP. (°C)	Cu-RICH PHASE (vol.%)	ANTI-MICROBIAL PROPERTY
KIND	C	Si	Mn	Ni	Cr	N	Cu	Nb	Ti	OTHERS			
K 1	0.01	0.31	0.20	0.10	16.8	0.01	0.48	—	—	—	600	0.25	◎
K 2	0.01	0.31	0.20	0.10	16.9	0.01	1.00	0.37	—	—	700	0.46	◎
K 3	0.01	0.31	0.20	0.10	16.8	0.01	1.50	0.37	—	—	500	0.78	◎
K 4	0.01	0.31	0.20	0.10	16.7	0.01	2.02	0.87	—	—	800	2.02	◎
K 5	0.01	1.86	0.20	0.10	16.6	0.01	0.51	0.37	—	—	700	0.31	◎
K 6	0.07	1.86	0.33	0.22	16.2	0.02	1.00	—	0.05	B: 0.02	700	0.30	◎
K 7	0.06	1.02	0.30	0.21	16.1	0.01	1.55	—	0.45	B: 0.01	700	0.55	◎
K 8	0.01	0.33	1.77	0.11	23.5	0.01	2.77	—	0.82	—	800	1.72	◎
K 9	0.01	0.20	0.21	0.10	11.0	0.01	1.01	—	—	Mo: 2.69	700	0.22	○
K10	0.01	0.20	0.20	0.09	13.1	0.01	1.00	—	—	Al: 0.81	700	0.28	○
K11	0.01	0.29	0.22	0.10	13.0	0.01	1.51	—	—	V: 0.90	600	0.81	◎
K12	0.01	0.30	0.20	0.10	12.8	0.02	1.02	—	—	Zr: 0.79	600	0.44	◎
K13	0.01	0.31	0.21	0.10	28.1	0.01	1.48	—	—	REM: 0.02	700	0.29	○

TABLE 2: THE EFFECT OF THE COMPOSITION OF FERRITIC STAINLESS STEEL AND AGING TREATMENT ON PRECIPITATION RATIO OF Cu-RICH PHASE AND ANTI-MICROBIAL PROPERTY (COMPARATIVE EXAMPLES)

STEEL KIND	ALLOYING COMPONENTS (wt.%)										AGING TEMP. (℃)	Cu-RICH PHASE (vol.%)	ANTI-MICROBIAL PROPERTY
	C	Si	Mn	Ni	Cr	N	Cu	Nb	Ti	OTHERS			
K14	0.01	0.27	0.22	0.11	11.2	0.01	0.01	—	—	—	no	0.02	×
K15	0.01	0.30	0.20	0.11	16.6	0.01	0.01	0.37	—	—	no	0.01	×
K16	0.01	0.31	0.20	0.10	16.5	0.01	0.27	0.35	—	—	no	0.07	△
K 1	0.01	0.31	0.20	0.10	16.8	0.01	0.48	—	—	—	no	0.05	△
K 2	0.01	0.31	0.20	0.10	16.9	0.01	1.00	0.37	—	—	no	0.08	△
K 3	0.01	0.31	0.20	0.10	16.8	0.01	1.50	0.37	—	—	400	0.07	△
K 4	0.01	0.31	0.20	0.10	16.7	0.01	2.02	0.87	—	—	900	0.18	△
K17	0.06	0.46	0.30	0.21	16.3	0.01	0.01	—	0.01	B: 0.01	500	0.07	×
K18	0.06	0.42	0.31	0.15	16.5	0.01	0.25	—	0.01	B: 0.01	600	0.06	×

It is noted from Table 1 that the ferritic stainless steel containing 0.4 wt.% or more Cu and having the structure that the Cu-rich phase was precipitated in the matrix at the ratio of 0.2 vol.% or more exhibited excellent anti-microbial function.

On the other hand, the test pieces K14 to K16 in Table 2 containing Cu not more than 0.4 wt.% had the Cu-rich phase precipitated at a smaller ratio and showed poor anti-microbial function. As for the test pieces K1 and K2 contain-

ing Cu in approximately same amount but not subjected to the aging treatment for the precipitation of the Cu-rich phase, it is noted that anti-microbial property was slightly improved, but sufficient anti-microbial property was not obtained. Even when the steel contains Cu in amount of 0.4 wt.% or more, anti-microbial function was changed in response to the temperature of aging treatment. In short, the precipitation of the Cu-rich phase was not more than 0.2 vol.% in the test piece K3 aged at 400°C or the test piece K4 aged at 900 °C, and any of these test pieces showed poor anti-microbial property. The test pieces K17 and K18 aged in the temperature range defined by this invention showed poor anti-microbial property, too, since Cu content was insufficient in these steel.

Example 2:

Austenitic stainless steel each having the composition shown in Table 3 was melted in a 30 kg-vacuum melting furnace, forged, hot rolled, annealed and then aged. The hot-rolled annealed sheets obtained in this way were repeatedly subjected to cold-rolling and annealing, so as to finally produce annealed cold-rolled sheets of 0.7 mm in thickness. The steel sheets which had not been aged after hot-rolling were aged after final annealing. The aging treatment after hot-rolling or final annealing was continuted 100 hrs.

Test pieces obtained from those sheets were observed by a transmission electron microscope to quantitatively measure the precipitation of the Cu-rich phase. The anti-microbial property of each steel was testified and evaluated by the same way as that in Example 1.

Each evaluation result together with the precipitation of the Cu-rich phase is shown in Table 3. It is noted that any of the test pieces No. 1-13 containing 1.0 wt.% or more Cu and having the Cu-rich phase precipitated at the ratio of 0.2 vol.% or more exhibited excellent anti-microbial property.

On the other hand, the test piece No. 18 which was not subjected to the aging treatment although containing 1.0 wt.% or more Cu had the Cu-rich phase precipitated at the ratio less than 0.2 vol.% and poor anti-microbial property. The precipitation of the Cu-rich phase was reduced below 0.2 vol.%, when the steel was aged at a temperature lower than 500°C or higher than 900 °C, as noted in the test pieces Nos. 15-17. These results means that Cu content in amount of 1.0 wt.% or more and the precipitation of the Cu-rich phase at the ratio of 0.2 vol.% or more are necessary for the improvement of anti-microbial property, and that the aging treatment at 500-900 °C is necessary to increase the precipitation of the Cu-rich phase at the ratio of 0.2 vol.% or more.

TABLE 3: THE EFFECT OF COMPOSITION OF AUSTENITIC STAINLESS STEEL AND CONDITIONS OF HEAT TREATMENT ON PRECIPITATION OF Cu-RICH PHASE AND ANTI-MICROBIAL PROPERTY

NOTE	TEST No.	ALLOYING ELEMENT (wt.%) C	Si	Mn	Ni	Cr	N	Cu	OTHERS	AGING TREATMENT PERIOD	Temp. (°C)	PRECIPITATION OF Cu-RICH PHASE (vol.%)	ANTI-MICROBIAL PROPERTY
PRESENT INVENTION	1	0.06	0.48	1.50	8.2	18.2	0.01	1.05	—	after final annealing	700	0.21	○
	2	0.02	1.50	1.98	7.8	16.0	0.02	1.93	—	after final annealing	700	0.23	○
	3	0.04	0.59	1.73	9.4	18.2	0.02	3.07	—	after hot rolling	800	0.42	◎
	4	0.01	0.11	0.77	11.8	16.9	0.01	3.99	—	after final annealing	900	1.78	◎
	5	0.01	0.20	1.10	20.0	25.8	0.01	4.88	—	no	—	1.23	◎
	6	0.06	0.42	1.47	8.2	18.2	0.02	2.99	Nb: 0.66	after hot rolling	750	0.77	◎
	7	0.05	0.50	1.50	8.2	18.2	0.03	2.98	Ti: 0.52	after final annealing	700	0.82	◎
	8	0.04	0.22	4.51	7.0	13.5	0.01	2.50	Mo: 2.50	after final annealing	800	0.67	○
	9	0.02	0.20	0.21	8.3	18.2	0.01	2.50	Al: 0.88	after final annealing	700	0.56	○
	10	0.04	0.50	1.25	8.2	18.3	0.02	2.99	Zr: 0.91	after hot rolling	700	0.88	◎
	11	0.04	0.44	1.51	8.2	18.2	0.01	3.69	V: 0.89	after hot rolling	700	0.91	◎
	12	0.01	0.51	4.20	7.9	19.0	0.01	2.50	B: 0.01	after final annealing	550	0.44	○
	13	0.02	0.50	1.02	8.0	18.2	0.01	3.22	REM:0.01	after hot rolling	600	0.39	◎
COMPARATIVE EXAMPLES	14	0.05	0.45	1.01	8.2	18.2	0.02	0.50	—	after final annealing	800	0.01	×
	15	0.02	1.50	1.98	7.8	16.0	0.02	1.93	—	after final annealing	950	0.01	×
	16	0.04	0.53	1.73	9.4	18.2	0.02	3.07	—	after hot rolling	950	0.04	×
	17	0.04	0.53	1.73	9.4	18.2	0.02	3.07	—	after hot rolling	400	0.12	△
	18	0.01	0.11	0.77	11.8	16.9	0.01	3.99	—	no	—	0.05	×

Example 3:

Martensitic stainless steel each having the composition shown in Table 4 was melted in a 30 kg-vacuum melting

furnace, forged, and then hot rolled. The hot-rolled sheets obtained in this way were annealed at 500-900 °C, while changing heating times variously in the range of 1 hour or longer. Thereafter, the annealed sheets were cold rolled to 1.5 mm in thickness and continuously annealed at 700-900°C within the time of 10 minutes or shorter as final annealing. In Table 4, the group A represents stainless steels containing 0.4 wt.% or more Cu according to the present invention, while the groupd B represents stainless steels containing Cu less than 0.4 wt.%.

TABLE 4

COMPOSITIONS OF MARTENSITIC STAINLESS STEELS USED IN EXAMPLE 3										
NOTE	STEEL KIND	ALLOYNG COMPONENTS (wt.%)								
		C	Si	Mn	Ni	Cr	N	Cu	Mo	V
PRESENT INVENTION	A 1	0.31	0.55	0.55	0.10	12.8	0.03	0.55	-	-
	A 2	0.33	1.54	0.54	0.10	13.0	0.03	1.54	-	-
	A 3	0.40	0.51	0.60	0.11	12.9	0.03	3.00	-	-
	A 4	0.35	0.55	0.55	0.10	13.1	0.02	4.42	-	-
	A 5	0.02	0.50	0.60	0.10	11.8	0.02	0.81	-	-
	A 6	0.02	0.51	0.75	0.11	12.0	0.02	2.05	-	-
	A 7	0.02	2.55	0.51	0.11	11.9	0.01	3.55	-	-
	A 8	0.01	0.33	0.61	0.11	12.1	0.01	2.77	3.25	-
	A 9	0.02	0.52	0.53	0.10	12.2	0.02	3.01	-	0.61
	A10	0.40	0.54	0.64	0.09	13.1	0.02	2.50	2.55	-
	A11	0.31	0.49	0.52	0.10	13.0	0.03	2.51	-	0.78
COMPARATIVE EXAMPLES	B 1	0.30	0.54	0.51	0.11	13.2	0.02	0.31	-	-
	B 2	0.41	0.49	0.56	0.10	13.0	0.03	0.25	1.35	-
	B 3	0.35	0.51	0.50	0.09	13.1	0.03	0.27	-	0.55
	B 4	0.02	0.49	0.55	0.10	11.9	0.01	0.34	-	-
	B 5	0.01	0.51	0.50	0.11	12.0	0.01	0.30	0.47	-
	B 6	0.01	0.41	0.52	0.08	11.8	0.01	0.25	-	0.45

A test piece obtained from each steel sheets was observed by a transmission electron microscope to quantitatively measure the precipitation of Cu-rich phase. The anti-microbial property of each test piece was examined and evaluated by the same way as that in Example 1.

The evaluation result together with the precipitation of the Cu-rich phase is shown in Table 5. It is noted that any of the test piece Nos. 1-11 (Group A) exhibited excellent anti-microbial property, since the steels contained 0.4 wt.% or more Cu with the precipitation of Cu-rich phase at the ratio of 0.2 vol.% or more.

On the other hand, the steels of the Group-B having lower Cu content showed poor anti-microbial property, since the precipitation ratio of the Cu-rich phase was less than 0.2 vol.% even when the hot-rolled steel sheets were annealed at 500-900°C. When the annealing temperature was lower than 500°C or higher than 900 °C, the Cu-rich phase was precipitated at the ratio less than 0.2 vol.% resulting in poor anti-microbial property nevertheless Cu content.

TABLE 5

THE EFFECT OF ANNEALING TEMPERATURE FOR HOT ROLLED SHEET ON THE PRECIPITATION OF Cu-RICH PHASE AND ANTI-MICROBIAL PROPERTY							
PRESENT INVENTION				COMPARATIVE EXAMPLE			
KIND	ANNEAL TEMP. (°C)	Cu-RICH PHASE (vol.%)	ANTI-MICROBIAL PROPERTY	KIND	ANNEAL TEMP. (°C)	Cu-RICH PHASE (vol.%)	ANTI-MICROBIAL PROPERTY
A 1	650	0.25	○	B 1	850	0.01	X
A 2	750	0.46	◎	B 2	800	0.01	X
A 3	800	0.78	◎	B 3	850	0.07	△
A 4	850	2.02	◎	B 4	800	0.05	△
A 5	850	0.31	○	B 5	850	0.08	△
A 6	800	0.45	◎	B 6	800	0.07	△
A 7	750	0.65	◎	A 4	950	0.12	△
A 8	700	1.32	◎	A 4	450	0.05	X
A 9	550	0.42	◎	A 7	950	0.08	△
A10	750	0.73	◎	A 7	480	0.02	X
A11	800	0.81	◎	A 8	950	0.07	△
				A10	480	0.03	X

Table 6 shows the relationship between the ratio of the Cu-rich phase precipitated in a steel sheet finally annealed according to the present invention and the evaluation of anti-microbial property. It is noted that the Cu-rich phase remained effectively in the durability of anti-microbial property, when the steel sheet containing 0.4 wt.% or more Cu was finally annealed at 700-900°C after being subjected in a hot rolled state to annealing at 500-900°C.

On the other hand, even in the case where a hot rolled sheet had been annealed at 500-900°C, the precipitation of the Cu-rich phase in the steel sheet containing Cu in amount less than 0.4 wt.% (B1-6 in Table 7) which was continuously annealed at 700-900°C was less than 0.2 vol.% resulting in poor anti-microbial property, since Cu content in the steel was short. In the case of the steel sheets containing enough Cu (A4, 7 and 8 in Table 7) where the temperature for annealing the hot rolled sheet was lower than 500 °C or higher than 900°C, the precipitation of the Cu-rich phase in the steel sheet finally annealed at 700-900 °C did not reach 0.2 vol.% resulting in poor anti-microbial property, since the final annealing was continuous and shor in time.

A test piece obtained by annealing a hot rolled steel sheet A4 6 hrs. at 750 °C, cold rolling it and then annealing it 1 minute at 750 °C was observed by SEM-EDX. The test piece had the metallurgical structure that Cu-rich phase precipitates were uniformly and minutely dispersed in the matrix. The stainless steel having said structure was excellent in anti-microbial property.

TABLE 6

THE EVALUATION OF ANTI-MICROBIAL PROPERTY OF ANNEALED COLD-ROLLED MARTENSITIC STAINLESS STEEL (THE PRESENT INVENTION)				
STEEL KIND	ANNEALING TEMP. FOR HOT ROLLED SHEET (°C)	ANNEALING TEMP. FOR COLD ROLLED SHEET (°C)	Cu-RICH PHASE (vol.%)	ANTI-MICROBIAL PROPERTY
A 1	650	900	0.22	○
A 2	750	900	0.36	◎
A 3	800	850	0.65	◎
A 4	850	850	2.02	◎
A 5	850	800	0.31	○
A 6	800	800	0.45	◎
A 7	750	900	0.65	◎
A 8	700	900	1.32	◎
A 9	550	850	0.42	◎
A10	750	800	0.73	◎
A11	800	800	0.81	◎

TABLE 7

THE EVALUATION OF ANTI-MICROBIAL PROPERTY OF ANNEALED COLD-ROLLED MARTENSITIC STAINLESS STEEL (COMPARATIVE EXAMPLES)				
STEEL KIND	ANNEALING TEMP. FOR HOT ROLLED SHEET (°C)	ANNEALING TEMP. FOR COLD ROLLED SHEET (°C)	Cu-RICH PHASE (vol.%)	ANTI-MICROBIAL PROPERTY
B 1	850	850	0.02	X
B 2	800	850	0.01	X
B 3	850	800	0.05	Δ
B 4	800	800	0.02	X
B 5	850	750	0.07	Δ
B 6	800	750	0.08	Δ
A 4	950	750	0.07	Δ
A 4	450	850	0.04	X
A 7	950	900	0.05	X
A 7	450	850	0.02	X
A 8	950	800	0.04	X
A10	480	800	0.03	X

According to the present invention as afore-mentioned, the anti-microbial property of stainless steel itself is farely improved by controlling Cu content in the steel material and the precipitation ratio of the Cu-rich phase in the matrix. Since the anti-microbial function is derived from material itself, the stainless steel keeps its excellent anti-microbial func-

tion for a long time. Consequently, the stainless steel is useful as material in various fields requiring sanitary environments, e.g. kitchen goods, devices or tools useful at a hospital, interior parts for building and grips or poles for tansportation vehicles such as busses or electric cars with which many and unspecified persons come into contact.

Claims

1. A stainless steel excellent in anti-microbial property containing 0.4-5.0 wt.% Cu and having the structure that a secondary phase mainly composed of Cu is precipitated at the ratio of 0.2 vol.% or more in the matrix.

2. A method of manufacturing a stainless steel excellent in anti-microbial property comprising the steps of:

   - providing a stainless steel containing 0.4-5.0 wt.% Cu, and
   - heating said stainless steel at 500-900 °C for a time enough to precipitate a secondary phase mainly composed of Cu at the ratio of 0.2 vol.% or more in the matrix.

3. A ferritic stainless steel excellent in anti-microbial property, having the composition containing 0.1 wt.% or less C, 2 wt.% or less Si, 2 wt.% or less Mn, 10-30 wt.% Cr, 0.4-3 wt.% Cu and the balance being essentially Fe, and the structure that a secondary phase mainly composed of Cu is precipitated at the ratio of 0.2 vol.% or more in the matrix.

4. The ferritic stainless steel defined in Claim 3 further containing 0.02-1 wt.% Nb and/or Ti.

5. The ferritic stainless steel defined in Claim 3 or 4 further containing at least one of Mo up to 3 wt.%, Al up to 1 wt.%, Zr up to 1 wt.%, V up to 1 wt.%, B up to 0.05 wt.% and rare earth metals up to 0.05 wt.%.

6. A method of manufacturing a ferritic stainless steel excellent in anti-microbial property comprising the steps of:

   - preparing a ferritic stainless steel having the composition containing 0.1 wt.% or less C, 2 wt.% or less Si, 2 wt.% or less Mn, 10-30 wt.% Cr, 0.4-3 wt.% Cu, optionally one or more selected from the group of 0.02-1 wt.% Nb and/or Ti, Mo up to 3 wt.%, Al up to 1 wt.%, Zr up to 1 wt.%, V up to 1 wt.%, B up to 0.05 wt.% and rare earth metals up to 0.05 wt.%., and the balance being essentially Fe,
   - cold-rolling said ferritic stainless steel,
   - finally annealing the cold-rolled steel sheet, and
   - aging the annealed steel sheet at 500-800 °C so as to precipitate secondary phase mainly composed of Cu at the ratio of 0.2 vol.% or more in the matrix.

7. An austenitic stainless steel excellent in anti-microbial property having the composition containing 0.1 wt.% or less C, 2 wt.% or less Si, 5 wt.% or less Mn, 10-30 wt.% Cr, 5-15 wt.% Ni, 1.0-5.0 wt.% Cu and the balance being essentially Fe, and the structure that a secondary phase mainly composed of Cu is precipitated at the ratio of 0.2 vol.% or more in the matrix.

8. The austenitic stainless steel defined in Claim 7 further containing one or more of 0.02-1 wt.% Nb and/or Ti, Mo up to 3 wt.%, Al up to 1 wt.%, Zr up to 1 wt.%, V up to 1 wt.%, B up to 0.05 wt.% and rare earth metals (REM) up to 0.05 wt%.

9. A method of manufacturing an austenitic stainless steel excellent in anti-microbial property comprising the steps of:

   - preparing an austenitic stainless steel having the composition containing 0.1 wt.% or less C, 2 wt.% or less Si, 5 wt.% or less Mn, 10-30 wt.% Cr, 5-15 wt.% Ni, 1.0-5.0 wt.% Cu, optionally one or more of 0.02-1 wt.% Nb and/or Ti, Mo up to 3 wt.%,Al up to 1 wt.%, Zr up to 1 wt.%, V up to 1 wt.%, B up to 0.05 wt.% and rare earth metals up to 0.05 wt.%, and the balance being essentially Fe,
   - hot-rolling said atustenitic stainless steel, and
   - heat treating the steel sheet at least one time at a temperature in the range of 500-900 °C so as to precipitate a secondary phase mainly composed of Cu at the ratio of 0.2 vol.% or more in the matrix, and

10. A martensitic stainless excellent in anti-microbial property having the composition containing 0.8 wt.% or less C, 3 wt.% or less Si, 10-20 wt.% Cr, 0.4-5.0 wt.% Cu and the balance being essentially Fe, and the structure that a secondary phase mainly composed of Cu is precipitated at the ratio of 0.2 vol.% or more in the matrix.

11. The martensitic stainless steel defined in Claim 10 further containing one or two of 4 wt.% or less Mo and 1 wt.% or less V.

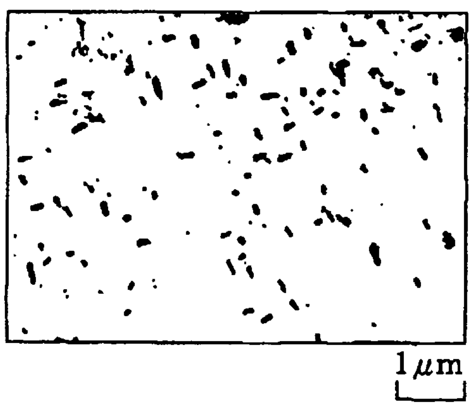
12. A method of manufacturing a martensitic stainless steel excellent in anti-microbial property comprising the steps of:

- preparing a martensitic stainless steel having the composition containing 0.8 wt.% or less C, 3 wt.% or less Si, 10-20 wt.% Cr, 0.4-5.0 wt.% Cu, and optionally one or two of Mo up to 4 wt.% and V up to 1 wt.%, and the balance being essentially Fe,
- hot-rolling said martensitic stainless steel
- annealing the hot-rolled steel sheet, and
- subjecting the annealed steel sheet to the batch-type annealing wherein said steel sheet is heated at 500-900 °C for one hour or longer so as to precipitate a secondary phase mainly composed of Cu at the ratio of 0.2 vol.% or more in the matrix.

13. The method defined in Claim 12 further involving the steps of:

- cold-rolling the steel sheet after the batch-type annealing, and then
- continuously annealing the cold-rolled steel sheet at 700-900 °C.

FIG.1



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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 649 915 A (NIPPON KOKAN KK) 26 April 1995 * Claim 1; page 5, line 36 - page 6, line 14 * ---	1,2	C22C38/16 C22C38/20 C22C38/42 C21D6/00
X	EP 0 478 790 A (NISSHIN STEEL CO LTD) 8 April 1992 * Claim 1; Table 1 * ---	3-5	
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 154 (C-1040), 26 March 1993 & JP 04 318153 A (TOUHOKU TOKUSHIYUKOU KK), 9 November 1992, * Table 2 * * abstract * ---	3-5	
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 373 (C-391), 12 December 1986 & JP 61 166953 A (NIPPON KOKAN KK), 28 July 1986, * Table 1; Fig.1 * * abstract * ---	7-9	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C C21D
X	EP 0 255 106 A (MAI EDELSTAHL) 3 February 1988 * Claims 2 and 3; Sample 1 of Table 1 * ---	3-5,7,8	
X	EP 0 384 317 A (NIPPON STEEL CORP) 29 August 1990 * Claims 1 and 7; Table 1 * ---	10-12	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	13 March 1997	Bjoerk, P

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 334 (C-0964), 21 July 1992 & JP 04 099128 A (NIPPON STEEL CORP), 31 March 1992, * Table 1 * * abstract * -----	10,11	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	13 March 1997	Bjoerk, P

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